

# Monofluorinated analogues of polychlorinated biphenyls (F-PCBs) - standards for analysis: retention behaviour in gas chromatography and MS characteristics

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## Introduction

Polychlorinated biphenyls (PCBs) have been the subject of a broad range of studies and investigations, because they are persistent organic pollutants (POPs). There is a concern about the health effects of PCB exposure. PCBs are structurally similar to polychlorinated dibenzodioxines (PCDDs) and polychlorinated dibenzofuranes (PCDFs) as well as to polybrominated dibenzoethers (PBDEs).

Their abundance as pollutants stems from their worldwide manufacture as heavy-used industrial chemicals. The overwhelming problem with PCBs is their continuing environmental impact; their persistence, and widespread prior use has caused global contamination of soil, rivers and other waterways that can affect our food and water supplies. The high lipophilicity causes accumulation in body lipids and liver organs, and subsequent bioaccumulation in the food chain.

Therefore, they have to be determined very frequently at the trace level in, *e.g.* water, food, sediment and soil. The sample preparation and final determination may well lead to systematic and non-systematic (random) errors. It is generally accepted that the accurate determination of micro contaminants in such complex mixtures requires the use of external or, preferably, internal standards (ISs). The benefit of using ISs with physico-chemical properties similar to those of the target compounds, is that both types of errors will be minimized.

While preliminary work on monofluorinated polycyclic aromatic hydrocarbons (F-PAHs) as ISs in gas chromatography (GC) was very promising [1], we recently synthesized a series of monofluorinated PCBs (F-PCBs). We found that they are a very promising set of internal standards for trace-level analysis of PCBs and are alternatives to <sup>13</sup>C-labelled analogues. In the present study, we focused attention on the retention behavior of F-PCBs in GC, and MS characteristics, with the intention to use them as calibration standards for GC-MS and electron capture detection (GC-ECD).

## Materials and Methods

### *Chemicals*

The following F-PCBs were synthesized [2], the numbers behind the names refer to the official numbers of the corresponding parent PCBs: 3'-fluoro-2,4,4'-trichlorobiphenyl (28), 2'-fluoro-2,4,6-trichlorobiphenyl (30), 3'-fluoro-2,4,6-trichlorobiphenyl (30), 4'-fluoro-2,4,6-trichlorobiphenyl (30), 3'-fluoro-2,4',5-trichlorobiphenyl (31), 3-fluoro-2,2',4,4'-tetrachlorobiphenyl (47), 3-fluoro-2,2',4',5-tetrachlorobiphenyl (49) and 3-fluoro-2,2',5,5'-tetrachlorobiphenyl (52).

### *GC-MS*

Analyses of three mixtures, PCBs, F-PCBs and PCBs with the corresponding F-PCBs, were carried out on a HP 6890 (Hewlett Packard, Palo Alto, CA, USA) gas chromatograph with MS detection. Briefly, 1- $\mu$ l volumes of the samples were injected. Separation was performed on a Restek XTI-5 capillary column (30 m  $\times$  0.25 mm I.D., 0.25  $\mu$ m film thickness). Helium was used as the carrier gas at a column head pressure of 97 kPa. The split flow was 120 ml/min. The split less time was 1.5 min. The column temperature was programmed from 103°C (4.5 min) to 280°C at 12°C/min. The final temperature was held for 20 min.

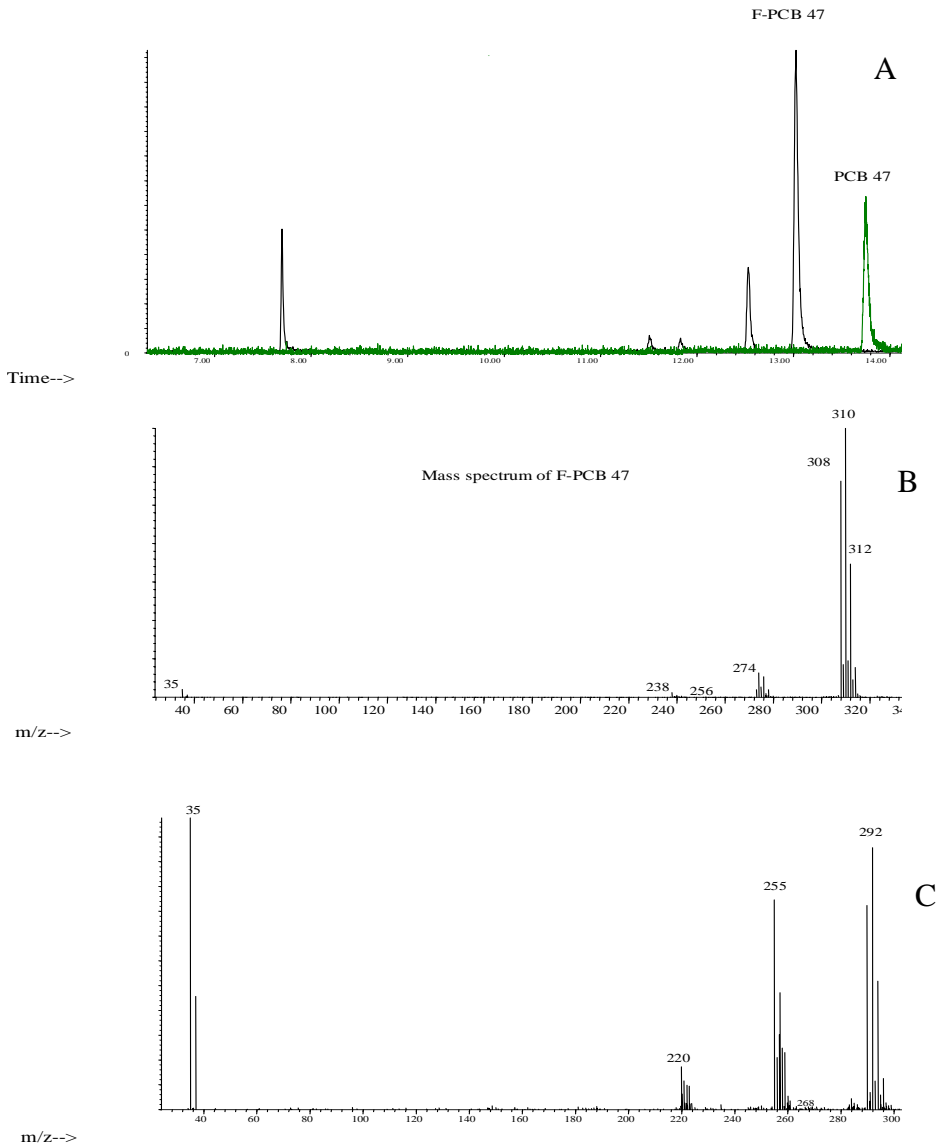
Detection was based on the simultaneous registration, at the appropriate retention time, of the signals corresponding to the two  $m/z$  values selected for each analyte.

## Results and discussion

The unusually small but administrable effect of fluorine monosubstitution on the properties of aromatic hydrocarbons, like F-PCBs, can be qualitatively understood by considering the influence of a fluorine atom on an aromatic system. First, fluorine induces a dipole moment, though not as strong as one might expect. The small fluorine atom is too small (hard) to retain the complete electron charge. In addition, hyperconjugation caused by overlap of the aromatic  $\pi$ -orbitals and the free fluorine p-orbitals, results in a partial transfer of the charge back to the aromatic system [1,3]. Secondly, as regards intermolecular interactions, as a result of the reduced polarisability, the London forces are less strong for F-PCBs than for the parent PCBs. The latter effect is antagonistic to the effect of an increased permanent dipole moment and is of similar magnitude. Consequently, the overall effect of fluorine substitution has two antagonistic effects: the creation of a permanent dipole moment and the reduction of the London forces. As a result, F-PCBs are surprisingly similar to their corresponding parent PCBs in terms of physico-chemical properties. A simple model of the electronic effects of fluorine substitution is shown in Fig. 1.



# GAS CHROMATOGRAPHY MASS SPECTROMETRY



**Fig. 2:** GC–MS of the F-PCB/PCB pair of the congener (47), 50 ng/mL each in *iso*-octane. Conditions:  $m/z$  35–400; for other details, see Materials and Methods.

As shown in the Fig. 2 (A) on the F-PCB/PCB pair of the congener (47), F-PCBs in general have shorter or identical retention times because they are slightly more non-polar. The reduction of the London force is variable compensated by the introduction of the permanent dipole moment. This depends on the pattern of fluorine substitution.

Based on the fluorine substitution in *ortho*-, *meta*- or *para*-position, the retention behaviour compared to the corresponding parent PCBs is different. This can be shown on the congener (30) with three different fluorination patterns: 2'-fluoro-2,4,6-trichlorobiphenyl (30), 3'-fluoro-2,4,6-trichlorobiphenyl (30) and 4'-fluoro-2,4,6-trichlorobiphenyl (30). Fluorine substitution in the *para*-positions, results in very close or even co-elute with their corresponding parent PCBs. The permanent dipole moment caused by fluorine in the *para* position is the strongest. Here, the compensation of the reduction of the London force is almost reached. The F-PCB congeners which are substituted in the *meta*-positions, overlap not of just slightly with the corresponding parent PCBs. The F-PCBs fluorine substituted congeners in the *ortho*-positions show much shorter retention times. This has two reasons. First the impact of the permanent dipole moment is the weakest in this position. Secondly, the conformation is changed partly by steric hindrance.

The figures 2 (B) and (C) show the MS spectra of the F-PCB/PCB pair of the congener (47). The most abundant ions for the congener pairs were to be found the  $[M]^+$ ,  $[M-Cl]^+$  and  $[M-Cl_2]^+$ . The difference between the molecule ions of the F-PCBs/PCB pairs is  $m/z$  18. Interestingly, the intensity of the  $[M-Cl]^+$  and  $[M-Cl_2]^+$  ions of the F-PCBs were in all cases, lower than that of the corresponding non-fluorinated PCB. Fluorine causes both, an +M and -I effect. The aromatic system is extended by hyperconjugation with the overlapping p-orbitals of fluorine, which causes additional stabilization of the charge in the F-PCBs. This leads to a slightly higher stability of the C-Cl bindings as well.

In this paper, the behavior of F-PCBs - which were synthesized by us - in GC-MS, is discussed for the first time. The main conclusion is that mono-substitution with fluorine causes only slight differences in retention behavior. Mainly depending on the *ortho*-, *meta*- or *para* position of fluorine substitution we observe complete or partial co-elution or separation of each F-PCB/PCB pair. This opens the way to use ECD instead of or in addition to MS. Furthermore, the difference between the molecule ions of the F-PCBs/PCB pairs is  $m/z$  18, which allows a simultaneous detection without separation using MS in the electron impact (EI) mode. Further, the MS spectrum of the F-PCBs shows less fragmentation intensity which makes them more valuable for quantification purposes.

F-PCBs are valuable internal standards, especially for the analysis with MS and ECD. Only the F-PCBs can be separated by retention time from the corresponding parent PCBs, and  $^{13}C$ -PCBs are, therefore, not useful in ECD. The use of F-PCBs as ISs is much more cost-consciously in comparison with  $^{13}C$  labelled analogous as well.

Ongoing investigations show, that the use of F-PCBs as ISs causes a highly desirable improved precision in PCB analysis. Additional studies with dynamic  $^{19}F$  nuclear magnet resonance spectroscopy ( $^{19}F$ -NMR) and solid state-NMR provide us with information concerning the dynamic of planarity and can be useful for toxicological studies.

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